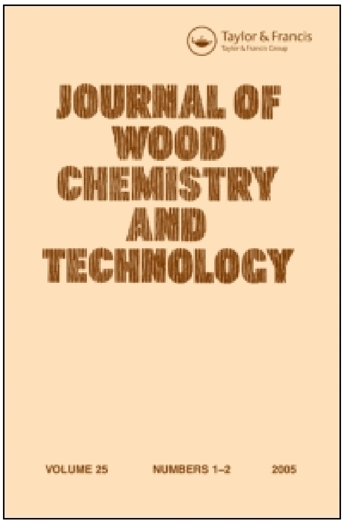

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1,1-Diarylethanes : Novel Compounds from Alkali Spent Liquors

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1,1-DIARYLETHANES : NOVEL COMPOUNDS FROM ALKALI SPENT LIQUORS

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ABSTRACT

Five 1,1-diarylethanes were detected in three industrial alkali pulping spent liquors. Of these, two were novel compounds. The methylmethine linkages present in these compounds is expected to have formed during pulping. The degraded lignin and residual lignin in the pulp can therefore also be expected to contain methylmethine linkages.

INTRODUCTION

Large quantities of unused by-product alkali lignin are produced by the chemical pulping industry. In order to uncover any potential commercial applications of the lignin, a systematic study of the chemical properties of industrial soda anthraquinone (AQ) lignin, soda bagasse lignin and pine kraft lignin was undertaken. As a result, it was shown that soda bagasse lignin can be used successfully in phenol formaldehyde thermosetting and coldset adhesives, both containing substantially higher levels of lignin than previously employed for similar products[1].

In the course of the study, a total of five 1,1-diarylethanes were detected in the three spent liquors. Two of these were novel compounds. In this paper, the occurrence of the diarylethanes in alkali spent liquors and their formation via a general reaction are discussed.

RESULTS AND DISCUSSION

Extracts of the three spent liquors were separately subjected to gas chromatography-mass spectrometric (GC-MS) analysis of the acetylated extracts. Alternatively the extracts were subjected to preparative high pressure liquid chromatography (HPLC) and the homogenous compounds thus obtained identified by spectroscopic methods (see Experimental). The yields of the respective compounds were obtained either directly or by quantitative GC analysis (see Experimental). A summary of the diarylethanes occurring in the three spent liquors is listed in Table 1.

The diarylethanes listed in Table 1 were observed for the first time in industrial spent liquors. Indeed, diarylethanes 4 and 5 proved to be novel compounds. Identification of 4 and 5 followed from spectral data,

TABLE 1

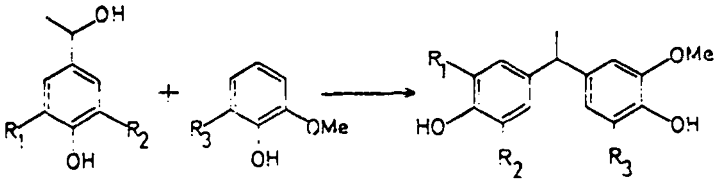
1,1-Diarylethanes present in industrial alkali spent liquors

SPENT LIQUOR	DIARYL ETHANE	YIELD BASED ON LIGNIN (%)	IDENTIFICATION
Soda bagasse	1 $RCH(CH_3)R$	low	GC-MS
	2 $RCH(CH_3)R'$	0.04	GC-MS
	3 $R'CH(CH_3)R'$	0.12	GC-MS
	4 $R'CH(CH_3)R''$	0.11	GC-MS
	5 $R''CH(CH_3)R''$	0.01	GC-MS
Kraft pine	3 $R'CH(CH_3)R'$	0.04	GC-MS
Soda/AQ Eucalyptus	4 $R'CH(CH_3)R''$	0.35	Isolation and spectral analysis
	5 $R''CH(CH_3)R''$	0.61	Isolation and spectral analysis

R = 4-hydroxyphenyl-
R' = 4-hydroxy-3-methoxyphenyl-
R" = 4-hydroxy-3,5-dimethoxyphenyl-

their structures were futhermore proved by comparison with independently obtained synthetic material. Similarly, a synthetically prepared standard of diaryl ethane 3 also aided its structural identification. The structures of 1 and 2 were, however, assigned by mass spectral analysis only and should therefore be considered as tentative.

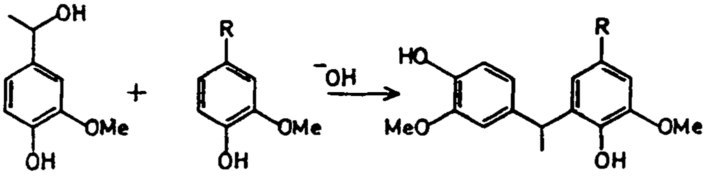
The independent synthesis of the new compounds 4 and 5 and that of the known bisguaiacylethane 3 was done by the alkali catalysed condensation of an appropriate benzyl alcohol with a relevant phenol as follows:



6 R_1 = H, R_2 = OMe	8 R_3 = H	3 R_1 = R_3 = H, R_2 = OMe
6 R_1 = H, R_2w = OMe	9 R_3 = OMe	4 R_1 = R_2 = OMe, R_3 = H
7 R_1 = R_2 = OMe	9 R_3 = OMe	5 R_1 = R_2 = R_3 = OMe

It is envisaged that the diarylethanes observed in the spent liquors were formed via a similar route. Mildly pulped pine kraft spent liquors for example contain the methylbenzyl alcohol 6[2]. It was, however, absent in the presently investigated kraft spent liquor[3]. Its disappearance can be attributed to its condensation with phenols such as the relatively abundant guaiacyl to give the observed 1,1-diarylethane 3.

Apart from the above observed condensation, the benzyl alcohols can also be expected to react with reactive 1,1-diarylethanes to give trimers, tetramers etc. Furthermore it may also react with larger lignin fragments. The isolation of the methylmethine linked diaryl compounds thus clearly suggests that more such methine linkages should occur in the alkali lignins. The residual lignin remaining in the pulp can therefore also be expected to contain such linkages. The condensation of methyl benzyl alcohols during alkali pulping can therefore be generalized as in Figure 1.



The methylmethine linkages can be expected to be stable against alkali degradation during pulping. The degraded lignin fragments and the residual lignin in the pulp can therefore be expected to resist further degradation if the methylmethine linkage content increases to significantly higher levels.

EXPERIMENTAL

Melting points were obtained on a Kofler micro hot-stage and are reported uncorrected. Infrared spectra recorded on a Beckman Acculab spectrophotometer, were obtained on solutions in spectroscopical chloroform. 'H-nmr spectra were determined on a Bruker WP-80 spectrometer in deuterated chloroform with tetramethylsilane as internal standard. Mass spectra, including accurate mass measurements, were determined with a Varian MAT-212 mass spectrometer with direct probe insertion, operated with an ionizing potential of 70 eV. Elemental analyses were done by the National Chemical Research Laboratory of the CSIR, Pretoria. Qualitative thin layer chromatography was done on Merck (Kieselgel 60 F_{254}) plates and column chromatography on Merck Kieselgel 60 (0.063 - 0.200 nm).

Three industrial spent liquors were extracted for 16 days on a liquid ether extraction apparatus. These were

- a kraft spent liquor (338 g, 49.4 % solids) obtained from the pulping (18 % active alkali, 23 % sulphidity) of *Pinus patula* to give pulp with a kappa number of 40;
- a soda spent liquor (800 g, 17.6 % solids) obtained from the pulping (15 % active alkali) of sugarcane bagasse yielding a pulp with a kappa number of approximately 10;
- a soda/AQ spent liquor (800 g, 26.7 % solids) obtained from the pulping (17 % active alkali) of *Eucalyptus grandis* yielding a pulp with a kappa number of about 22.

The extracts were dried ($MgSO_4$), their solvents removed and a portion of each was acetylated (acetic anhydride/pyridine).

GC-MS analysis of the acetylated extracts were done on an SE-30 capillary column (50 m, 0.32 mm ID, 50 μm phase thickness) with a probe on column injector. Helium was used as carrier gas at a linear flow speed of 25 cm/s. A VG 7070 mass spectrometer was used to obtain mass spectra every 1.5 seconds.

Quantitative GC analyses were done on the same column used above with an FID detector and 3,4-dimethoxybenzaldehyde as internal standard. The 1,1-diarylethanes detected in the different spent liquors are listed in Table 1. Other compounds detected in the spent liquors will be communicated elsewhere^4.

The novel compounds 4 and 5 were subsequently purified from the soda/AQ spent liquor by chromatography. A portion of the extract (6.64 g) was chromatographed on Prepak-500 silica cartridge packed with 325 g of high quality porous silica on a Waters Prep L-System 500 A HPLC. Ethyl acetate hexane (20:50 to 100:0) was used as eluent at a pump speed of 100 ml/min. This was followed by final purification on a Knaurr modular high pressure liquid chromatograph on a Knaurr Lithosorb EHG (7 g) column at a pump rate of 10 ml/min with the same eluent.

The above isolation technique afforded the 1,1-diarylethanes; 4-[1-(4-hydroxy-3-methoxyphenyl)ethyl]-2,6-dimethoxphenol (4): υ_{max} ($CHCl_3$), 3550 (OH) 2980, 2950 & 2855 (C-H), 1620 (C=C,Ar), 1505, 1460, 1330, 1270 to 1190, 1120 & 1035 cm^{-1}; δ ($CDCl_3$) 1.54 & 1.62 (d, 3H, J = 7.4 Hz, $-CH-CH_3$), 3.83 (S, 3H, $O-CH_3$), 3.84 (s, 6H, $-O-CH_3$), 4.0 (q, 1H, J = 7.4 Hz, -CH-), 6.43 (s, 2H, Ar-H), 6.66 to 6.97 (m, 3H, Ar'-H); m/e (%) 305 (M^+ + 1, 10), 304 (M^+, 52), 289 ($M^+ -CH_3$, 100 %), 246 (12), 181 (8), 151 (6); [Found 304.1310; $C_{17}H_{20}O_5$ requires 304.1311]; $[\alpha]^{25}$ = 0($CHCl_3$, c = 1.0) and 4-[-hydroxy-3,5-dimethoxypheny]ethyl]-2,6-himethoxyphenol (5): υ_{max} ($CHCl_3$) 3550 (sharp, O-H), 2950, 2850 (C-H), 1610 (C=C, Ar), 1460, 1360, 1325, 1115, 900 cm^{-1}; δ ($CHCl_3$), 1.54 & 1.63 (d, 3H, J = 7.3 Hz, $-CH-CH_3$), 3.84 (s, 12H, $-O-CH_3$), 4.0 (q, 1H, J = 7.3 Hz, -CH-), 5.45 (s, 2H, Ar-O-H), 6.43 (s, 4H, Ar-H); m/e (%) 334 (M^+, 42 %), 320 (19), 319 (M^+-CH_3, 86), 181 (70), 151 (22); [Found 334.1418; $C_{18}H_{22}O_6$ requires 334.1416].

Synthesis of 3, 4 and 5

3,5-Dimethoxy-4-hydroxyphenylethanol (7) (0,415 g, 2.10 mmol) and 2,6-dimethoxyphenol (9) (0.534 g, 3.47 mmol) were dissolved in water (25 ml) containing sodium hydroxide (0,40 g). After refluxing for two hours, the mixture was cooled, acidified (dil. HCl) and extracted with ether (4 x 60 ml). The combined ether extracts were dried ($MgSO_4$) and the solvent evaporated. Preparative HPLC of a portion of the crude product on a Lichrosorb EH6 column with ethyl acetate-hexane 1:1 as solvent afforded 5 in 64 % yield. The infrared, 'H-nmr and mass spectra of this compound were identical with that of 5 isolated from the spent liquor. Acetylation of 5 (0.10 g) with acetic anhydride (0.5 ml) and pyridine (0.5 ml) overnight afforded pure 4,4'ethylidene bis-[2,6-dimethoxyphenyl acetate] after crystallization from ethyl acetate and hexane; mp 184 to 185 °C; [Found C 63.15, H 6.12. $C_{22}H_{26}O_8$ requires C 63.15; H 6.26].

The above method was also used to prepare 4 from 4-hydroxy-3-methoxyphenylethanol (6) (0.373 g) and 2,6-dimethoxyphenol (9) (0.342 g). After semi-preparative HPLC with ethyl acetate : hexane (1:1), 4 was isolated in 25 % yield. Spectral analysis was again identical to that of the compound isolated from the spent liquor. Subsequent acetylation (as before) and reprecipitation in ether/hexane afforded the amorphous diacetate of 4, mp 78 to 81 °C; [Found C 64.98; H 6.29. $C_{21}H_{24}O_7$ requires C 64.94; H 6.23].

The dimer 3 was prepared by the alkali catalyzed reaction of 4-hydroxy-3-methoxy phenylethanol (7) (1.54 g) with guaiacol 8 (1.24 g) in water (20 ml) containing sodium hydroxide (1.00 g). After three hours refluxing, work up and preparative chromatography (ethyl acetate hexane, 1:1) as before the symmetrical dimer 3 was obtained in a 23 % yield. υ_{max} ($CHCl_3$) 3550 (O–H), 2850 - 2900, 1610, 1500, 1200 - 1280; $\delta_{(CDCl_3)}$ 1.52 & 1.60 (d, 3H, J = 7 Hz, –CH(CH_3)–), 3.86 (s, 6H, –O–CH_3), 4.0 (q, 1H, J = 7 Hz, –CH(CH_3)–, 5.6 (s, 2H, D_2O exchangeable, ArOH), 6.6 - 6.9 (m, 6H, ArH). The synthetically prepared compound was used to verify the strucure of 3 in the kraft and soda bagasse spent liquor by GC (as before).

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